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## Dimerization and low-dimensional magnetism in nanocrystalline TiO<sub>2</sub> semiconductors doped by Fe and Co

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**Abstract.** The report is devoted to an analysis of the structural and magnetic state of the nanocrystalline diluted magnetic semiconductors based on TiO<sub>2</sub> doped with Fe and Co atoms. Structural and magnetic characterization of samples was carried out using X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), X-ray absorption spectroscopy (XAS), electron paramagnetic resonance (EPR) spectroscopy, SQUID magnetometry, and the density functional theory (DFT) calculations. Analysis of the experimental data suggests the presence of non-interacting paramagnetic Fe<sup>3+</sup> and Co<sup>2+</sup> ions in the high-spin state and negative exchange interactions between them. The important conclusion is that the distribution of dopants in the TiO<sub>2</sub> matrix, even at low concentrations of 3d-metal dopant (less than one percent), is not random, but the 3d ions localization and dimerization is observed both on the surface and in the nanoparticles core. Thus, in the paper the quantum mechanical model for describing the magnetic properties of TiO<sub>2</sub>:(Fe, Co) was suggested. The model operates only with two parameters: paramagnetic contribution of non-interacting 3d-ions and dimers having different exchange interactions between 3d magnetic carriers.

### 1. Introduction

This report is based on the results of investigation of the structure, the ground magnetic and electronic states of the refined nanocrystalline systems TiO<sub>2</sub>:(Co, Fe) with the anatase crystal structure taking into account the paramagnetic contribution, dimerization and dimensionality of the systems [1-3]. The study of magnetic properties was carried out on TiO<sub>2</sub>:(Fe, Co) samples containing 3d impurities with less than 6 at.% of 3d-atoms just after the sol-gel synthesis and etching. The etching aimed to remove the foreign phases and segregations to exclude the external factors, which could be influenced on the magnetic properties. The matrix of TiO<sub>2</sub> is chemically inert to the acid treatment so this matrix can be a convenient model object for the study of the magnetic properties of TiO<sub>2</sub> doped by Fe and Co, caused by the intrinsic nature of magnetism. The density functional theory (DFT) calculations are applied to determine the 3d spin states and character of the band structure. Besides, the DFT approach allows revealing the type of solid solution, in particular, substitutional or interstitial ones in TiO<sub>2</sub>

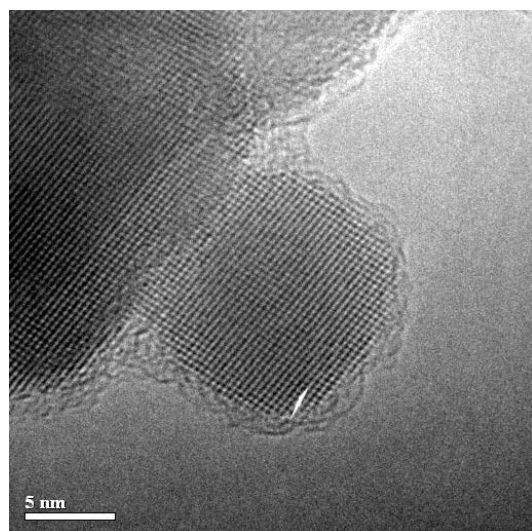


matrix doped by different 3d-metals. Besides that, the DFT modelling can calculate the most favorable configurations for 3d-ions complexes (e.g., dimerization).

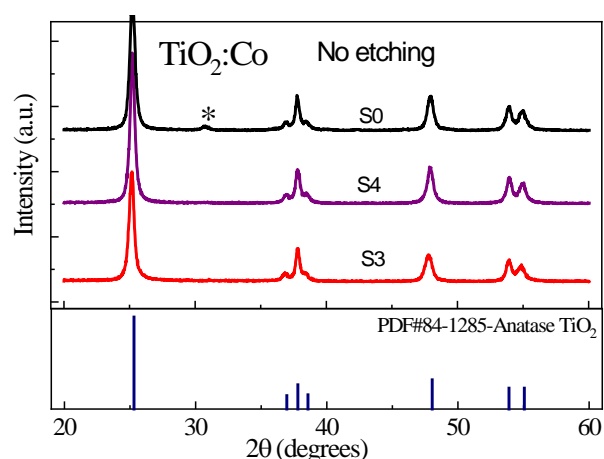
## 2. Experimental Results and Discussion

### 2.1. Electron Microscopy and XRD analysis of the samples

Figure 1 shows the typical high-resolution transmission electron microscopy (HRTEM) of  $\text{TiO}_2\text{:Co}$  nanoparticles in the initial state after synthesis.



**Figure 1.** HRTEM pictures of the sample  $\text{TiO}_2\text{:Co}$ . The disordered regions on the particle surface are observed.



**Figure 2.** X-ray diffraction patterns of  $\text{TiO}_2\text{:Co}$  samples in as-prepared state. Samples for X-ray analysis were not etched. The asterisk in the patterns indicates the traces of the brookite phase.

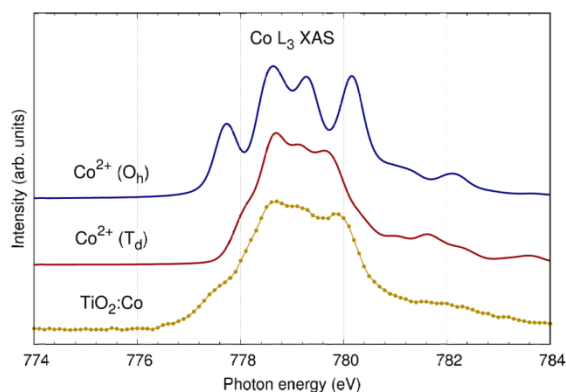
The average size of  $\text{TiO}_2$  nanoparticles, estimated from the HRTEM pictures (figure 1) is about 20 nm. The nanoparticle's core does not contain a significant number of defects (for example, interfaces and dislocations). Independently from Co content on the particle's surface after preparation, the disordered surface layers are observed (figure 1). The origin of this disordered layer is unclear. One can only assume that synthesis under relatively non-equilibrium conditions at low temperature did not allow forming kinetically a perfect surface of the nanoparticles. Another origin of disordered layers would be an excess accumulation of impurities and defects in these areas.

Figure 2 presents X-ray diffraction patterns of samples obtained immediately after synthesis with the different  $\text{TiO}_2\text{:Co}$  compositions, including the non-doped sample. The samples for XRD analysis were not etched. It should be noted that the etching of the samples preserves their structural state (X-ray diffraction patterns are not shown). It can be seen that all samples after synthesis in the indicated composition range contain mainly the anatase phase, while the sample with a low content of cobalt the traces of the brookite phase is also observed (marked with an asterisk).

So, X-ray diffraction studies did not reveal any extraneous phases in the samples just after synthesis. The sizes of coherently scattering domains (CSD) estimated from the line width for all samples are in the range (15–20) nm. The approximate correspondence of the sizes of nanoparticles at HRTEM observation with CSD indicates that the nanoparticles are mostly single crystals, which is confirmed by the HRTEM data. To investigate the intrinsic properties, it was essential do not exceed the limit of Co solubility in  $\text{TiO}_2$  matrix to avoid the appearance of undesirable foreign phases and segregations as it was mentioned in [3].

## 2.2. X-ray absorption spectroscopy

Figure 3 shows crystal-field multiplet calculations of Co  $L_3$  XAS spectra with the charge-transfer process for  $\text{Co}^{2+}$  ions in oxygen octahedral ( $\text{O}_h$ ) and tetrahedral ( $\text{T}_d$ ) environments and experimental Co  $L_3$  XAS spectra of Co-doped  $\text{TiO}_2$  nanopowder. The crystal field and electron interactions determine the shape of Co  $L$  X-ray absorption spectra. The Co  $L_{2,3}$  XAS spectrum of Co-doped  $\text{TiO}_2$  nanopowder is well-described by calculation spectrum for  $\text{Co}^{2+}$  ions with tetrahedral ( $\text{T}_d$ ) oxygen coordination. However, we do not exclude a small part of the cobalt ions in octahedrally coordinated sites, which are indicated by the shoulder at energies from 777 to 778 eV.



**Figure 3.** Co  $L_3$  X-ray absorption spectra of and  $\text{TiO}_2\text{:Co}$  nanopowder. Charge-transfer multiplet calculations for  $\text{Co}^{2+}$  ions in the oxygen octahedral ( $\text{O}_h$ ) and tetrahedral ( $\text{T}_d$ ) environments.

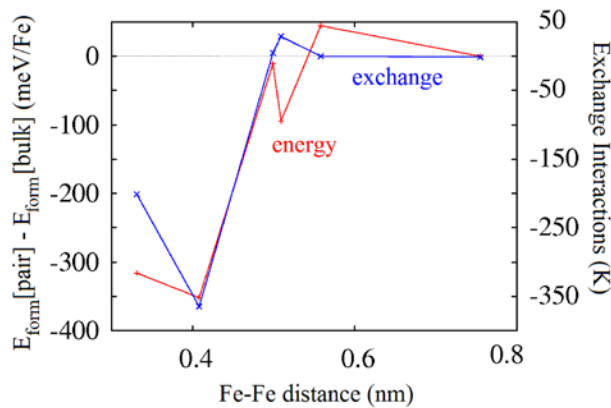
Summarizing the Co  $L$  XAS data we can conclude that Co ions are in the 2+ oxidation state. The coordination oxygen environment of  $\text{Co}^{2+}$  ions in Co-doped  $\text{TiO}_2$  nanoparticles is mainly tetrahedral ( $\text{T}_d$ ) [4]. It is essential to underline that the tetrahedral positions of Co can be located in both sites – interstitial and substitutional. Further, the density-functional theory calculations confirmed that the tetrahedrally coordinated cobalt in the interstitial positions is more energetically favorable in the anatase lattice.

## 2.3. The theoretical calculation of exchange interactions within Fe-Fe or Co-Co pairs on DFT-based model

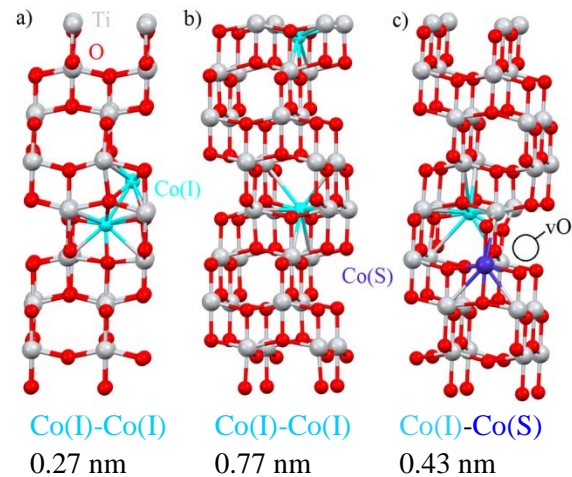
To quantitatively describe the magnetic properties of diluted magnetic semiconductors based on  $\text{TiO}_2\text{:}(\text{Fe}, \text{Co})$ , it is proposed to use a quantum mechanical model of non-interacting paramagnetic ions  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  and dimers ( $\text{Fe}^{3+}\text{--Fe}^{3+}$ ) and ( $\text{Co}^{2+}\text{--Co}^{2+}$ ) with different values of negative exchange interactions in pairs [5]. The model is based on the assumption, confirmed by the EPR data and density functional theory (DFT) calculations, that there are thermodynamically stable dimers ( $\text{Fe}^{3+}\text{--Fe}^{3+}$ ) in octahedral positions in the  $\text{TiO}_2$  system with  $\text{Fe}^{3+}$ . Thus, the most preferable configuration for iron-based dimers is realized for iron replacement in octahedral positions instead of titanium atoms, as it should be observed for the substitutional solution. Figure 4 demonstrates the magnitudes of exchange interactions in dimers as a function of the distance between  $\text{Fe}^{3+}$  ions. It was shown that the value of the exchange interactions inside the pair strongly depends on the distance between the iron ions (figure 4). The magnitude of the exchange interaction is maximal for the smallest distances between the iron atoms. In contrast to  $\text{TiO}_2\text{:Fe}$ , the Co-ions prefer to occupy, mainly, interstitial  $\text{TiO}_2$  lattice sites. Probably, due to the two-valent  $\text{Co}^{2+}$  ion state, an interstitial solution rather than substitutional one is preferably formed. As it is shown on figure 5, the most energetically favorable dimer configurations are the interstitial atoms (I+I) at distances of approximately 0.27 nm and 0.77 nm. A relatively low energy is also required for Co-configurations in which both interstitial atoms (I+I) with a vacancy (S+I+vO) are present simultaneously. It also turns out that tetrahedral positions can be the most favorable positions in these sites, as it follows from XAS studies [4]. Thus, the resulting interstitial solution based on  $\text{TiO}_2\text{:Co}$  also undergoes dimerization, but with a significantly larger set of energetically favorable dimers. Presumably, a more considerable amount of

dimer types may be required to describe the magnetic properties compared with the  $\text{TiO}_2$  system doped with iron. Besides that,  $\text{Co}^{2+}$  ions have a high spin state in the  $\text{TiO}_2$  system as it was shown by XAS investigation and DFT calculation.

Finally, it was demonstrated that the quantum mechanical model describes both the magnetization curves and the temperature dependence of magnetic susceptibility for all samples with a sufficient accuracy if one suggests the paramagnetic  $\text{Co}^{2+}$  or  $\text{Fe}^{3+}$  contributions and only two types of dimers ( $\text{Co}^{2+}\text{--Co}^{2+}$ ) or ( $\text{Fe}^{3+}\text{--Fe}^{3+}$ ) with the different magnitude of exchange interactions.



**Figure 4.** The difference between formation energy per iron atom of the pair and single iron atom (red line). The value of exchange integral as a function of the distance between iron-ions centers (blue line) in  $\text{TiO}_2$  doped by Fe.



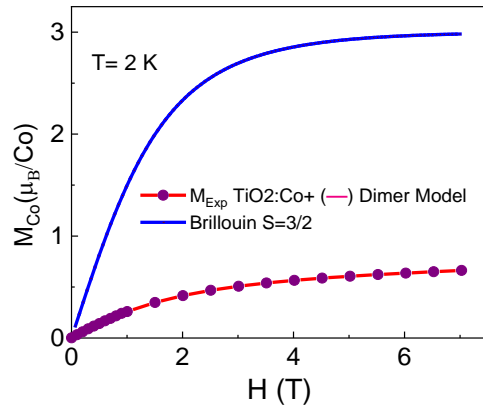
**Figure 5.** The optimized atomic structure of anatase  $\text{TiO}_2\text{:Co}$  with the most energetically favorable positions of Co–Co pairs in the interstitials (I) sites at short distance (a) and large distance (b); (c) the pair of Co-ions (interstitial (I) and substitutional (S)) with larger Co–Co distance in the vicinity of oxygen vacancy (vO). Co atom is marked by blue color, Ti - gray color, oxygen - red color.

#### 2.4. Magnetic Properties

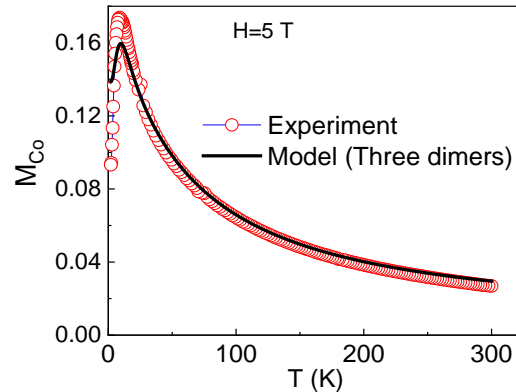
Figure 6 demonstrates the field dependencies of magnetization for sample  $\text{TiO}_2\text{:Co}$  with  $\sim 6$  at.% Co measured at 2 K. The magnetization is represented in the Bohr magnetons per cobalt atom, which allows us to directly estimate the deviation of the experimentally measured magnetic moment from the calculated value given by the Brillouin function for  $\text{Co}^{2+}$  atoms in the high-spin state with magnetic moment of  $3\mu_B$ . It can be seen that the Brillouin modeled magnetization curve exhibits a substantially higher magnetization value ( $3\mu_B/\text{Co}$ ) as it was observed experimentally for all samples. This difference between the value of high spin state ( $3\mu_B/\text{Co}$ ) and the experimentally measured value for high content of Co sample can reach the difference of 5 times. It is impossible to explain it suggesting the existence only the non-interacting  $\text{Co}^{2+}$  paramagnetic ions. The most likely reason for the relatively low magnetization, similar to  $\text{TiO}_2\text{:Fe}$  system [3], is the existence of cobalt dimers with negative exchange interactions in the  $\text{TiO}_2\text{:Co}$  compounds. Therefore, we can assume that dimers or short-range AFM correlations with negative exchange interactions can make a significant contribution to the magnetization process of systems  $\text{TiO}_2$  doped by Co. As one can see in figure 6, the magnetization curves are satisfactorily described by the approach of the quantum spin model. It can describe the experimental results using the combination of a paramagnetic contribution and only two types of dimers with the appropriated parameters of exchange interactions for those pairs (e.g.,



$J_1 = -15$  K,  $J_2 = -200$  K) and their corresponding contents in the system (figure 6 – experimental curve (wine dots) and the model description (red line)).



**Figure 6.** The experimental magnetization curves  $M_{\mu_B/Co}$  vs field at 2 K for sample  $TiO_2:Co$  (6 at.%) (solid wine dots) and the calculated Brillouin function (blue line) for the high spin state  $Co^{2+}$  with  $S=3/2$  ( $3\mu_B$ ). Red line is a quantum model description of an experimental curve (solid wine dots) with the following parameters: values of exchange interactions in two dimers -  $J_1 = -15$  K,  $J_2 = -200$  K. The content of dimers with  $J_1 \sim 42\%$ , 38% of dimers with  $J_2$  and 20% of paramagnetic  $Co^{2+}$  ions, respectively.



**Figure 7.** The experimental temperature dependence of the magnetization for sample  $TiO_2$  with  $\sim 6$  at.% Co (open red dots) without a paramagnetic contribution, measured at 5T. It was modelled by three types of dimers – ( $J_1 = -5$  K (16%),  $J_2 = -25$  K (33%) and  $J_3 = -300$  K (33%)) marked by a black line.

### 2.5. The experimental determination of dimer exchange interaction

One of the experimental evidence for the existence of dimers in the  $TiO_2:Co$  system could be the detection of the temperature maximum of magnetization as the temperature decreases. The behavior of the magnetization of dimers as a function of temperature for  $TiO_2:Co$  at low temperatures must differ from the behavior of a conventional antiferromagnetic. The magnetization should be decreased to zero below a specific critical temperature ( $T_{max}$ ). At first, Bleaney and Bowers [5] paid attention to this fact and explained this behavior by negative exchange interaction inside pairs. To separate the contribution of the dimers with negative exchange interactions to the temperature dependence of the magnetization for the samples and to establish the critical  $T = T_{max}$ , it is necessary to subtract the paramagnetic contribution.

Figure 7 shows the temperature dependence of the magnetization for the sample without a paramagnetic contribution (about 20%), measured at 50 kOe. The temperature dependence of the magnetization demonstrates a maximum about  $\sim 10$  K (figure 7). This  $T_{max}$  value for the spin  $S=3/2$  probably should correspond to some effective exchange interaction in the dimers with the minimal value of exchange interactions in the system. The estimated exchange interaction's values for dimers in the DFT model were found to be in reasonable agreement with the magnitude of exchange interactions evaluated by processing the magnetic measurements data (figure 7).

## 3. Conclusions

The refined nanocrystalline  $TiO_2:(Fe, Co)$ -based samples (Co or Fe up to 6 at.%) with an anatase structure after a sol-gel synthesis and subsequent etching were prepared. After the etching, the ferromagnetic contribution disappeared in the samples. Respectively, the magnetic properties of the

investigated samples cannot be described at the assumption of the existence only of the isolated paramagnetic ions of  $\text{Co}^{2+}$  or  $\text{Fe}^{3+}$  with spins  $S=3/2$  and  $S=5/2$ . To explain the magnetic properties of  $\text{TiO}_2(\text{Fe}, \text{Co})$  it is necessary to suggest the appearance of AFM contribution in all samples. The quantum-mechanical model takes into account the non-interacting 3d-ions and dimers with different negative exchange interactions, allow describing quite effectively the magnetic properties of the mentioned system. The model fits well to describe the magnetization curves and the temperature dependence of magnetic susceptibility of the  $\text{TiO}_2(\text{Fe}, \text{Co})$  samples with different contents of the single spins and two types of dimers. The EPR data confirm the existence of single spins and dimers in the  $\text{TiO}_2\text{Fe}$  systems at all investigated temperatures. It should be noted, that the description of the experimental data by a larger number of pairs may require the non-justified fitting with an arbitrary set of parameters.

Thus, the ground magnetic state of  $\text{TiO}_2(\text{Fe}, \text{Co})$  system can be successfully described by the mixed magnetic state consisting of uncoupled isolated paramagnetic 3d-ions and magnetically coupled 3d-ions with negative exchange interactions without ferromagnetic contribution that are typical for the low-dimensional system. Future studies are necessary to get the direct experimental evidence of the existence of magnetic clusters or dimers in the  $\text{TiO}_2$  matrix doped by Fe and Co to clarify the fundamental origin and formation of the magnetic complexes.

The obtained results of the research of low-dimensional magnetism in Fe- and Co-doped  $\text{TiO}_2$  may have a general nature and can be extended to a broad class of diluted magnetic semiconductors, for example, based on  $\text{ZnO}$ ,  $\text{In}_2\text{O}_3$ , and others.

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